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(21) International Application Number: PCT/US88/02541 (22) International Filing Date: 27 July 1988 (27.07.88) (31) Priority Application Number: 078,460 (32) Priority Date: 27 July 1987 (27.07.87) (33) Priority Country: US (60) Parent Application or Grant (63) Related by Continuation US 078,460 (CIP) Filed on 27 July 1987 (27.07.87) (71) Applicant (for all designated States except US): AMOCO CORPORATION [US/US]; Mail Code 1907, Patents and Licensing Department, P.O. Box 87703, Chicago, IL 60680-0703 (US).		(72) Inventor; and (75) Inventor/Applicant (for US only) : HARRIS, James, E. [US/US]; 80 Freemont Court, Somerset, NJ 08873 (US). (74) Agent: EARLE, Thomas, E.; Mail Code 1907, Patents and Licensing Department, Amoco Corporation, P.O. Box 87703, Chicago, IL 60680-0703 (US). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report.</i>
(54) Title: POLY(ARYL ETHER SULFONE) COMPOSITIONS HAVING IMPROVED FLOW PROPERTIES (57) Abstract <p>Described herein are immiscible poly(aryl ether sulfone) blends possessing improved flow properties. The novel compositions contain (a) from about 80 to about 99 percent by weight of a poly(aryl ether sulfone) having a second order glass transition temperature (T_g) higher than about 240°C, and (b) from about 1 to about 20 percent by weight of a second poly(aryl ether sulfone) having a T_g lower than about 225°C. The compositions described herein retain the very attractive characteristics of their constituents, and display excellent mechanical properties and heat resistance.</p>		

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POLY(ARYL ETHER SULFONE) COMPOSITIONS
HAVING IMPROVED FLOW PROPERTIES

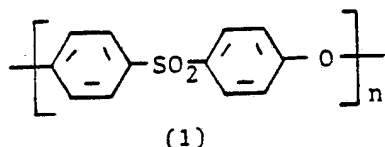
5 This is a continuation-in-part of U.S. Serial No.
07/078,460, filed July 27, 1987.

FIELD OF THE INVENTION

10 This invention is directed to immiscible poly(aryl
ether sulfone) blends possessing improved flow proper-
ties. The novel compositions contain (a) from about 80
to about 99 percent by weight of a poly(aryl ether sul-
15 (Tg) higher than about 240°C, and (b) from about 1 to
about 20 percent by weight of a second poly(aryl ether
sulfone) having a Tg lower than about 225°C. The compo-
sitions described herein retain the very attractive
characteristics of their constituents, and display
20 excellent mechanical properties and heat resistance.

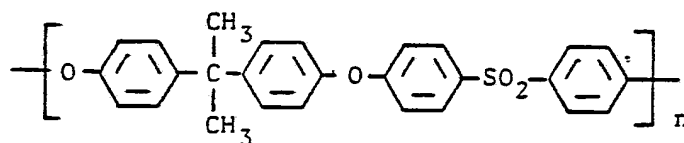
BACKGROUND OF THE INVENTION

 Poly(aryl ether sulfones) have been known for about
two decades; they are tough linear polymers that possess
25 a number of attractive features such as excellent high
temperature resistance, good electrical properties, and
very good hydrolytic stability. Two poly(aryl ether
sulfones) are commercially available. A poly(aryl ether
sulfone) is available from Imperial Chemical Industries
30 Limited. It has the formula (1)



35 and is produced by polycondensation of 4-(4'-chloro-
phenylsulfonyl)phenol, as described in British Patent
Specification No. 1,153,035. The polymer contains no

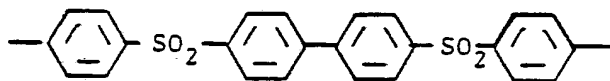
aliphatic moieties and has a heat deflection temperature of approximately 210°C. Another commercial poly- (aryl ether) is available from Amoco Performance Products, Inc. under the trademark UDEL®. It corresponds to formula (2) and has a heat deflection temperature of about 180°C.



(2)

Polymer (2) is prepared via the nucleophilic polycondensation reaction of 2,2-bis(4-hydroxy-phenyl) propane ("bisphenol-A") with 4,4'-dichlorodiphenyl sulfone. This method, described by Johnson et al., Journal of Polymer Science, A-1, Vol. 5, 1967, pp. 2415-2427, and Johnson et al., U. S. Patent Nos. 4,107,837 and 4,175,175, has been shown to be quite general and applicable for the synthesis of a broad range of other poly(aryl ether sulfones) (hereinafter called PAE's). Using this approach, a host of PAE's having wide ranging properties was prepared.

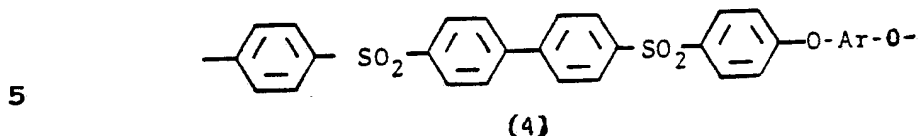
Materials (1) and (2) display relatively low glass-transition and, hence, low heat distortion temperatures. The drawback is serious, since it makes the two polymers unsuitable in applications where a high Tg is important. Such applications include, for example, the area of composites which often require a matrix capable of maintaining structural integrity at relatively high temperatures. Thus, over the years, numerous poly(aryl ether sulfones) having high Tg's have been prepared. Of particular interest among these latter polymers are those containing the 4,4'-bis(phenylsulfonyl)biphenyl units (3):



(3)

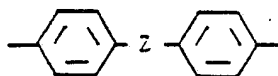
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Thus, U. S. Patent No. 3,647,751 depicts polymers of formula (4):



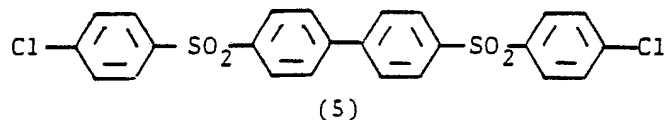
wherein Ar is defined as a diphenylene or naphthylene radical or a polynuclear divalent radical of the formula:

10

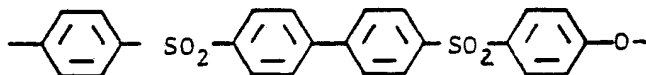


15 where Z is a divalent aliphatic, cycloaliphatic or arylaliphatic radical containing 1 to 8 carbon atoms or -O-, -S-, -SO-, -SO₂-, or -CO-.

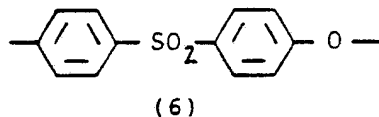
U. S. Patent No. 3,634,355 describes a number of polymers prepared from 4,4'-bis(4-chlorophenylsulphonyl)-
20 biphenyl (5).



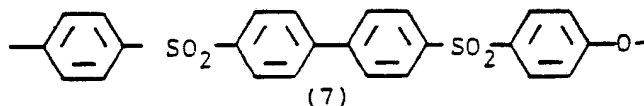
25 For instance, in Example 5 the following polymer is provided:



30 Example 16 depicts the polymer containing units (6) and (7) is a 4:1 molar ratio.



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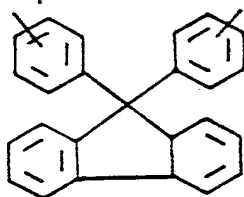
Example 17 shows the same structure, except that units (6) and (7) are present in a 1:1 ratio.

The homopolymer (7) is described in U. S. Patent No. 4,009,149.

5 Copolymers containing units (3) are also the subject of two patent applications (U.S. Serial numbers 701,234 and 701,306), both filed on February 13, 1985 in the names of James Elmer Harris, Louis Michael Maresca and Markus Matzner, both titled "Polyaryl Ether Sulfone
10 Polymers", and both commonly assigned.

Other poly(aryl ether sulfones) displaying high glass transition temperatures are, for example, those containing terphenylene, naphthylene, anthracenylene and fluorene-9,9-bis(phenylene) units (8):

15



20

(8)

The above listed high Tg materials have generally high melt viscosities and are difficult to melt-fabricate. The development of compositions with improved melt
25 flow properties and better melt-fabricability based on the aforementioned high Tg poly(aryl ether sulfones) is, therefore, of great practical importance. It is, of course, necessary that the novel compositions retain the attractive features of the original polymers. Products
30 satisfying the above listed criteria are the subject of the instant invention.

DESCRIPTION OF THE INVENTION

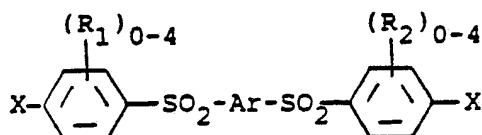
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It was now unexpectedly discovered that immiscible blends containing (a) from about 80 to about 99 percent

by weight, preferably from about 85 to about 98 percent by weight, of a poly(aryl ether sulfone) having a second order glass transition temperature (T_g) higher than about 240°C, and (b) from about 1 to about 20 percent by weight preferably from about 2 to about 15 percent by weight of a second poly(aryl ether sulfone) having a T_g lower than about 225°C, display vastly improved melt-flow properties. It is unexpected that the compositions retain the excellent mechanical properties of the constituents. Moreover, the heat distortion temperature of the high T_g material remains practically unaffected by the addition of the lower T_g polymer.

It is preferred that the two poly(aryl ether sulfones) be immiscible. A two-phase immiscible blend, is demonstrated by the blend having two distinct glass transition temperatures (T_g). One advantage of an immiscible blend having one higher and one lower T_g constituent is an improved flow since the lower T_g constituent tends to migrate to the wall and acts as a lubricant.

The poly(aryl ether sulfones) having second order glass transition temperatures greater than about 240°C are based on the monomers of formula (9) where X is a halogen, preferably chlorine or fluorine, or a hydroxyl group; Ar is a divalent aromatic radical selected from the group of

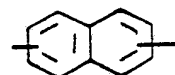
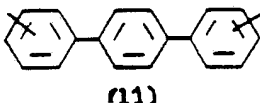
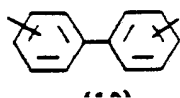


X = halogen or hydroxyl

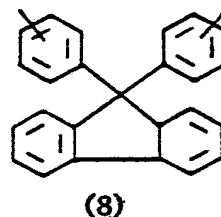
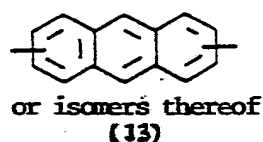
(9)

biphenylene (10), terphenylene (11), naphthylene (12), anthracenylene (13), and fluorene-9,9-bis(phenylene) (8);

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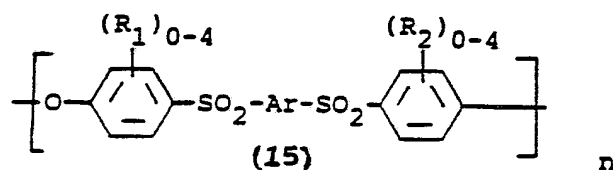
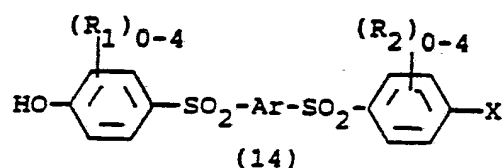


or isomers thereof



- 10 R_1 and R_2 are inert substituents such as hydrogen or C_1 to C_4 alkyl or alkoxy groups; they can be the same or different.

The high Tg poly(aryl ether sulfones) can be prepared by the nucleophilic polycondensation of (9) (X=halogen) with a dihydric phenol; the latter may be the dihydroxy variant of (9) (X=OH) or any other dihydric phenol or a mixture of these materials. Conversely, these high Tg polymers may be prepared by the nucleophilic polycondensation of (9) (X=OH) with any activated dihalobenzenoid compound or mixtures thereof. Note, that the base-catalyzed self-condensation of (14), where X is a halogen, is yet another route to the homopolymer (15).



- 35 The nucleophilic polycondensation of (14) with a dihydric phenol and an activated dihalobenzenoid compound, offers an additional route to these high Tg products. For the

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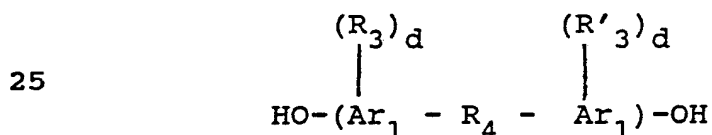
purposes of this invention it is essential that the high Tg materials contain at least 50 mole percent of units (15).

The dihydric phenols useful in the instant invention are preferably weakly acidic dinuclear phenols such as, for example, the dihydroxy-diphenyl alkanes or the nuclear halogenated derivatives thereof, such as, for example, the 2,2-bis(4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)2-phenyl ethane, bis(4-hydroxyphenyl)methane, or their chlorinated derivatives containing one or two chlorines on each aromatic ring. Other materials also termed appropriately bisphenols are also highly valuable and preferred. These materials are the bisphenols of a symmetrical or unsymmetrical joining group, as for example, ether oxygen

(-O-), carbonyl ($\text{-}\overset{\text{O}}{\parallel}\text{C-}$), sulfone ($\text{-}\overset{\text{O}}{\parallel}\text{S}\overset{\text{O}}{\parallel}\text{-}$), or hydrocarbon

residue in which the two phenolic nuclei are joined to the same or different carbon atoms of the residue.

Such dinuclear phenols can be characterized as having the structure:



wherein Ar₁ is an aromatic group and preferably is a phenylene group; R₃ and R'₃ can be the same or different inert substituent groups such as alkyl groups having from 1 to 4 carbon atoms, aryl, halogen atoms, i.e., fluorine, chlorine, bromine or iodine, or alkoxy radicals having from 1 to 4 carbon atoms; the d's are independently integers having a value of from 0 to 4, inclusive; and R₄ is representative of a bond between aromatic carbon atoms as in dihydroxy-diphenyl, or is a divalent radical,

including for example, radicals such as $\overset{\text{O}}{\parallel}\text{-C-}$, -O- , -S- ,
 -S-S- , -SO- , -SO_2 , and divalent hydrocarbon radicals such
as alkylene, alkylidene, cycloalkylene, cycloalkylidene,
5 or the halogen, alkyl, aryl or like substituted alkylene,
alkylidene and cycloaliphatic radicals as well as aroma-
tic radicals and radicals fused to both Ar_1 groups.

Examples of specific dihydric polynuclear phenols
include, among others, the bis-(hydroxyphenyl) alkanes
10 such as

2,2-bis-(4-hydroxyphenyl)propane,
2,4'-dihydroxydiphenylmethane,
bis-(2-hydroxyphenyl)methane,
bis-(4-hydroxyphenyl)methane,
15 bis(4-hydroxy-2,6-dimethyl-3-methoxyphenyl)-
methane
1,1-bis-(4-hydroxyphenyl)ethane
1,2-bis-(4-hydroxyphenyl)ethane,
1,1-bis-(4-hydroxy-2-chlorophenyl)ethane,
20 1,1-bis-(3-methyl-4-hydroxyphenyl)propane,
1,3-bis-(3-methyl-4-hydroxyphenyl)propane,
2,2-bis-(3-phenyl-4-hydroxyphenyl)propane,
2,2-bis-(3-isopropyl-4-hydroxyphenyl)propane,
2,2-bis-(2-isopropyl-4-hydroxyphenyl)propane,
25 2,2-bis-(4-hydroxy-naphthyl)propane,
2,2-bis-(4-hydroxyphenyl)pentane,
3,3-bis-(4-hydroxyphenyl)pentane,
2,2-bis-(4-hydroxyphenyl)heptane,
bis-(4-hydroxyphenyl)phenylmethane,
30 2,2-bis-(4-hydroxyphenyl)-1-phenyl-propane
2,2-bis-(4-hydroxyphenyl)1,1;1,3;3,3,-hexa-
fluoropropane and the like;

di(hydroxyphenyl) sulfones such as

bis-(4-hydroxyphenyl)sulfone,
35 2,4'-dihydroxydiphenyl sulfone,
5-chloro-2,4'-dihydroxydiphenyl sulfone,
5'-chloro-4,4'-dihydroxydiphenyl sulfone,

and the like;
di(hydroxyphenyl)ethers such as
bis-(4-hydroxyphenyl) ether,
the 4,3'-; 4,2'-; 2,2'-; 2,3'-dihydroxyphenyl
ethers,
4,4'-dihydroxy-2,6-dimethyldiphenyl ether,
bis-(4-hydroxy-3-isopropylphenyl) ether,
bis-(4-hydroxy-3-chlorophenyl) ether,
bis-(4-hydroxy-3-fluorophenyl) ether,
bis-(4-hydroxy-3-bromophenyl) ether,
bis-(4-hydroxynaphthyl) ether,
bis-(4-hydroxy-3-chloronaphthyl) ether, and
4,4'-dihydroxy-3,6-dimethoxydiphenyl ether.

Other useful diphenols are, for example, the naphthalenediols and the mononuclear diphenols such as hydroquinone or resorcinol. Dihydroxybiphenyls, such as 4,4'-biphenol, are also very useful.

In addition to the activated dihalobenzenoid compounds, dinitrobenzenoid compounds are also suitable for the purposes of the instant invention. Any dihalobenzenoid or dinitrobenzenoid compound or mixtures thereof can be employed in this invention which compound or compounds has the two halogens or nitro-groups bonded to benzene rings having an electron withdrawing group in at least one of the positions ortho or para to the halogen or nitro group. The dihalobenzenoid or dinitrobenzenoid compound can be either mononuclear, where the halogens or nitro groups are attached to the same benzenoid ring; or polynuclear where they are attached to different benzenoid rings, as long as there is an activating electron withdrawing group in the ortho or para position of that benzenoid nucleus. Fluorine and chlorine substituted benzenoid reactants are preferred; the fluorine compounds for fast reactivity and the chlorine compounds for their inexpensiveness. Fluorine substituted benzenoid compounds are most preferred, particularly when there is a trace of water present in

the polymerization reaction system. However, this water content should be maintained below about 1 percent and preferably below 0.5 percent for best results.

5 An electron withdrawing group is employed as the activator group in these compounds. It should be, of course, inert under the reaction conditions, but otherwise its structure is not critical. Preferred are the strongly activating groups such as the sulfone group

10 $\begin{array}{c} \text{O} \\ || \\ (-\text{S}-) \\ || \\ \text{O} \end{array}$, bonding two halogen or nitro-substituted benze-

noid nuclei, as in 4,4'-dichlorodiphenyl sulfone and 4,4'-difluorodiphenyl sulfone, although such other strong withdrawing groups hereinafter mentioned can also be used
15 with equal ease.

The more powerful of the electron withdrawing groups give the fastest reactions and hence are preferred. It is further preferred that the ring contain no electron supplying groups on the same benzenoid nucleus as the
20 halogen or nitro group; however, the presence of other groups on the nucleus or in the residuum of the compound can be tolerated.

The activating groups can be basically either of two
25 types:

(a) monovalent groups that activate one or more halogens or nitro-groups on the same ring such as another nitro or halo group, phenylsulfone, or alkylsulfone, cyano,
30 trifluoromethyl, nitroso, and hetero nitrogen, as in pyridine.

(b) divalent groups which can activate displacement of halogens on two different

35 rings, such as the sulfone group $\begin{array}{c} \text{O} \\ || \\ -\text{S}- \\ || \\ \text{O} \end{array}$; the

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carbonyl group $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$; the vinylene group $\begin{array}{c} \text{H} \\ | \\ -\text{C}=\text{C}- \\ | \\ \text{H} \end{array}$;

the sulfoxide group $\begin{array}{c} \text{O} \\ \parallel \\ -\text{S}- \end{array}$; the azo group $-\text{N}=\text{N}-$;

5

the saturated fluorocarbon groups $\begin{array}{c} \text{CF}_3 \\ | \\ -\text{C}- \\ | \\ \text{CF}_3 \end{array}$,

CF_2 $-\text{CF}_2\text{CF}_2$; organic phosphine oxides $\begin{array}{c} \text{O} \\ \parallel \\ -\text{P}- \\ | \\ \text{R}''_3 \end{array}$;

10

where R''_3 is a hydrocarbon group and the ethylidene group $\text{A}-\text{C}-\text{A}$ where A can be hydrogen or halogen.



The polyarylene polyether polymers of this invention are prepared by methods well known in the art as for instance the one-step reaction of a double alkali metal salt of a dihydric phenol with a dihalobenzenoid compound in the presence of specific liquid organic sulfoxide or sulfone solvents under substantially anhydrous conditions. Catalysts are not necessary for this reaction.

20

The polymers may also be prepared in a two-step process in which a dihydric phenol is first converted in situ in the primary reaction solvent to the alkali metal salt by the reaction with the alkali metal, the alkali metal hydride, alkali metal hydroxide, alkali metal alkoxide or the alkali metal alkyl compounds. Preferably, the alkali metal hydroxide is employed. After removing the water which is present or formed, in order to secure substantially anhydrous conditions, the dialkali metal salts of the dihydric phenol are admixed and reacted with the dihalobenzenoid or dinitrobenzenoid compound.

25

30

Additionally, the polyethers may be prepared by the procedure described in, for example, U. S. Patent No. 4,176,222 in which at least one bisphenol and at least one dihalobenzenoid compound are heated at a temperature of from about 100° to about 400°C with a mixture of

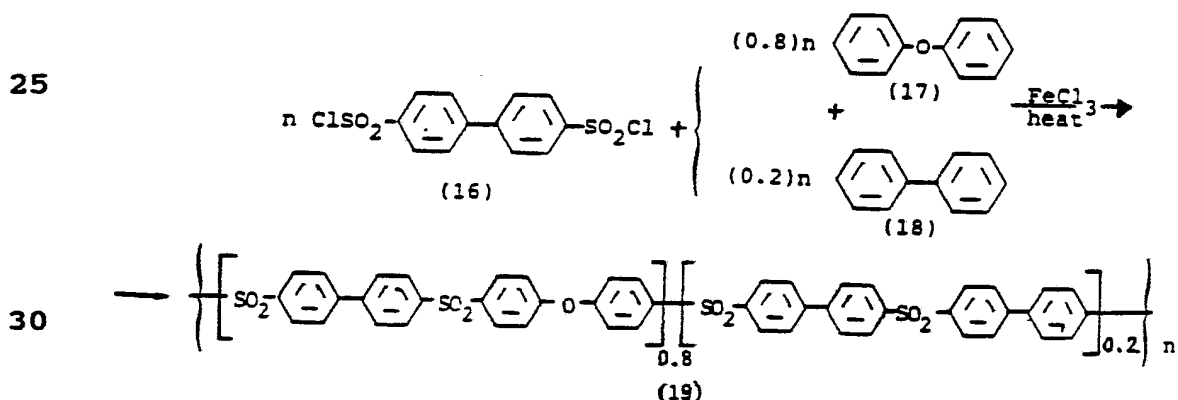
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sodium carbonate or bicarbonate and a second alkali metal carbonate or bicarbonate having a higher atomic number than that of sodium.

Further, the polyethers may be prepared by the
 5 procedures described in Canadian Patent No. 847,963 wherein the bisphenol and dihalobenzenoid compound are heated in the presence of potassium carbonate using a high boiling solvent such as diphenylsulfone.

Halophenols or nitrophenols wherein the halogen or
 10 nitro group is activated by an electron withdrawing group in the ortho- and/or para positions can also be used for the preparation of the poly(aryl ether sulfones). The halophenols or nitrophenols can be used alone or in conjunction with a diphenol and a dihalo- or dinitro-
 15 benzenoid compound as defined above.

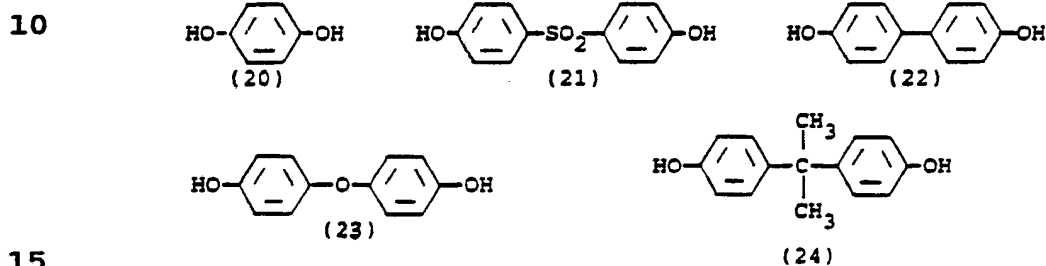
While the preparation of the high Tg poly(aryl ether sulfones) via the nucleophilic route is preferred, these materials may also be made via electrophilic (Friedel-Crafts) processes. These processes have been described
 20 in, for example, U. S. Patents Nos. 3,773,720; 3,321,449; 3,406,149; and 4,008,203; and in British Patent No. 1,060,546. A typical example is shown in Equation (I):



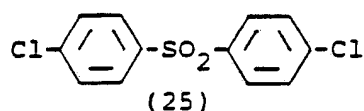
35 The electrophilic polymerizations are performed in the presence of typical Friedel-Crafts catalysts such as ferric chloride, aluminum chloride, ferric bromide, boron

trifluoride, and the like. A variety of solvents such as chlorinated hydrocarbons, nitrobenzene, arochlor, dimethyl sulfone, etc. are useful. Temperatures of up to 250°C, and even higher are preferably employed when high molecular weight polymers are desired.

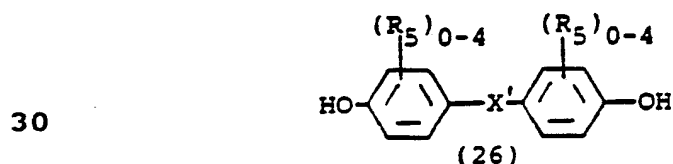
The preferred high T_g poly(aryl ether sulfones) are (19), and those based on (5) and the dihydric phenols (20), (21), (22), (23), and (24).



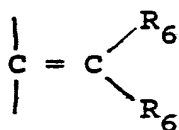
The poly(aryl ether sulfones) having second order glass transition temperatures lower than about 225°C are obtained by the nucleophilic polycondensation of 4,4'-dichlorodiphenyl sulfone (25) with



25 bisphenols of the formula (26):



wherein X' is selected from the group of hydrocarbon radicals such as alkylene and alkylidene radicals having up to and inclusive 8 carbon atoms, cycloalkylene and cycloalkylidene radicals having up to and inclusive 9 carbon atoms, and the radicals



5 the R₅'s are C₁ to C₄ alkyl or alkoxy radicals or halogen atoms and can be the same or different; the R₆'s are hydrogen or C₁ to C₄ alkyl radicals or halogen atoms; they can be the same or different.

The low Tg poly(aryl ether sulfones) are prepared using methods that are similar to those used for the preparation of their high Tg counterparts.

The preferred low Tg poly(aryl ether sulfone) is represented by formula (2).

The compositions of this invention are prepared by any conventional mixing method. For example, a preferred method comprises mixing the two poly(aryl ether sulfones) in powder or granular form in an extruder and extruding the mixture into strands, chopping the strands into pellets and molding the pellets into the desired article.

20 The compositions of this invention may include mineral fillers such as carbonates including chalk, calcite and dolomite; silicates including mica, talc, wollastonite, silicon dioxide; glass spheres; glass powders; aluminum; clay; quartz; and the like. Also, reinforcing fibers such as fiberglass, carbon fibers, and the like may be used. The compositions may also include additives such as titanium dioxide; thermal stabilizers, ultraviolet light stabilizers, plasticizers, and the like.

30 The compositions of this invention may be fabricated into any desired shape, i.e., moldings, coatings, films, or fibers. They are particularly desirable for use as electrical insulation for electrical conductors.

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EXAMPLES

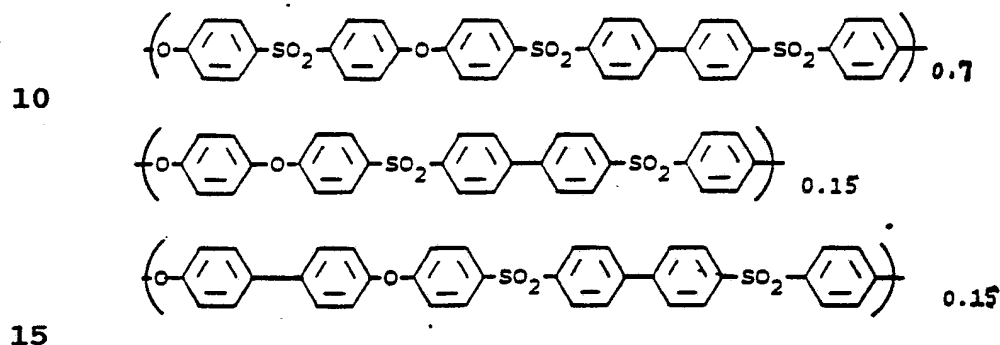
The following examples serve to give specific

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illustrations of the practice of this invention but they are not intended in any way to limit the scope of this invention.

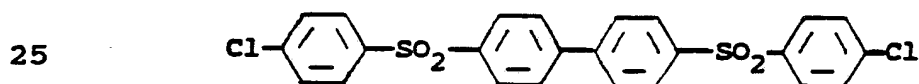
CONTROL A

A poly(aryl ether sulfone) random terpolymer of the following structure



was prepared as described below. Into a 500 ml flask provided with a stirrer, nitrogen inlet tube, thermometer, reflux condenser with a Dean-Stark trap and a dropping funnel were placed:

45.31 g (0.09 moles) of 4,4'-bis(p-chlorophenyl-sulfonyl)biphenyl,



15.77 g (0.063 moles) of 4,4'-dihydroxydiphenyl sulfone,

30

1.49 g (0.0135 moles) of hydroquinone,
2.51 g (0.0135 moles) of 4,4'-biphenol,
14.93 g (0.108 moles) of potassium carbonate, and
110.00 g of sulfolane.

35

A nitrogen atmosphere was maintained throughout the reaction. A small amount of monochlorobenzene (MCB) was

temperature reached about 145°C, the MCB started to distil entraining the water formed. A dropwise addition of MCB was maintained to replace the chlorobenzene which was distilling out. After about 1.25 hours, the temperature reached 190-210°C; it was maintained at that level for about 4 hours. Cooling was then begun. 55 g of MCB and 0.25 g of NaOH were added when the temperature reached 130°C. At 120°C, bubbling of CH₃Cl (to end-cap the polymer) was begun and continued for 0.5 hours. 90 ml of MCB were then added and the reaction mixture was cooled to room temperature.

The mixture was filtered and the filtrate was coagulated in excess methanol. The obtained polymer was dried until constant weight; its reduced viscosity (RV) was 0.5 dl/g (0.2 g/100 ml; 25°C, N-methylpyrrolidone).

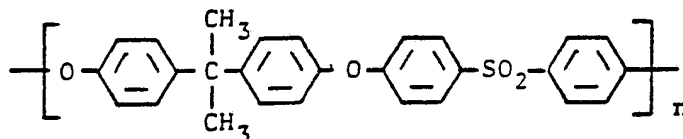
The material was fluxed in a Brabender Plasticorder mixer at 360°C for about 5 minutes. The melt flow index of the copolymer at 380°C and 44 psi was measured according to ASTM D1238 and is given in Table I. The copolymer resin was placed in a 4x4x0.020-inch cavity mold and compression molded in a South Bend hydraulic press whose jaws had been electrically heated to about 375°C. The 0.020-inch thick compression molded sheet was shear cut into one-eighth inch wide strips. The heat deflection temperature at 264 psi (ASTM D648) was estimated as follows:

The modulus-temperature curve and T_g were measured for specimens shear cut from the compression molded sheet according to the method described in Olabisi, et al., Polymer-Polymer Miscibility, Academic Press, NY, page 126. The HDT was taken as the temperature at which the tensile modulus dropped to 100,000 psi as described by M. T. Takemori, Soc. Plastics Eng., Proceedings of 36th ANTEC Conf., April 1978, pp. 216-219. The T_g and HDT are given in Table I.

EXAMPLE 1

85 weight percent of the poly(aryl ether sulfone) of Control A was mixed with 15 weight percent of polysulfone with a Tg of 185°C of the structure

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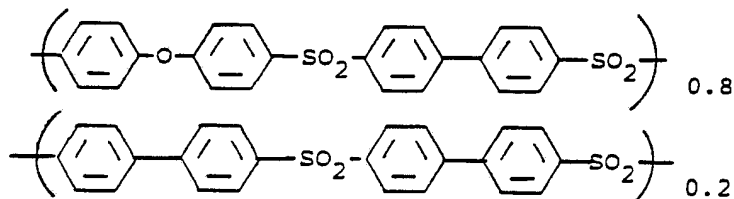
(UDEL[®] P3703 obtained from Amoco Performance Products, Inc.) in a Brabender Plasticorder mixer at 360°C for about 5 minutes. The blend was molded and tested as in Control A. The results are shown in Table I. The blend is immiscible as can be deduced from the existence of two Tg's. It is remarkable that the HDT remains unchanged even though the melt flow index was increased by a factor greater than two.

20

CONTROL B

A poly(aryl ether sulfone) random copolymer of the structure

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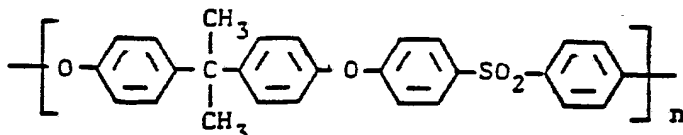
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(Astrel[®] 360 obtained from 3M Corporation) was fluxed in a Brabender Plasticorder at about 360 °C for about 5 minutes. The resin was molded and tested as in Control A. The results are given in Table I.

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EXAMPLE 2

85 weight percent of the poly(aryl ether sulfone) of Control B was mixed with 15 weight percent of polysulfone
 5 with a Tg of 185°C of the structure



10

(UDEL[®] P1700 obtained from Amoco Performance Products, Inc.) in a Brabender Plasticorder mixer at 360°C for
 15 about 5 minutes. The blend was molded and tested as in Control A. The results are shown in Table I. The blend is immiscible as evidenced by its two Tg's. Again, the HDT remains the same, while there is a considerable increase in the melt-flow value of the blend.

20

TABLE I

	<u>Control A</u>	<u>Example 1</u>	<u>Control B</u>	<u>Example 2</u>
25 Melt Flow Index @ 380°C (g/10 min)	0.61*	1.38*	11.6**	26.3**
Tg (°C)	255	250, 180	285	285, 180
30 HDT (°C)	240	240	275	275

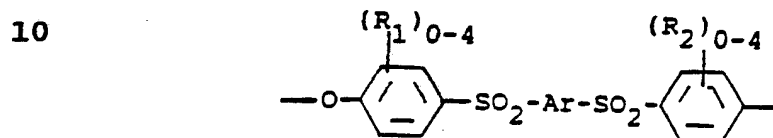
* measured at 44 psi.

** measured at 440 psi.

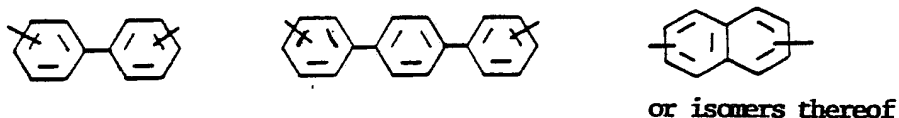
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WHAT IS CLAIMED IS:

1. A poly(aryl ether sulfone) composition having improved flow properties comprising an immiscible blend of (a) from about 80 to about 99 percent by weight of a poly(aryl ether sulfone) having a second order glass transition temperature (T_g) higher than about 240°C, which consists essentially of units of the formula:



- 15 wherein Ar is selected from the group of:



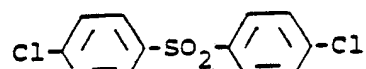
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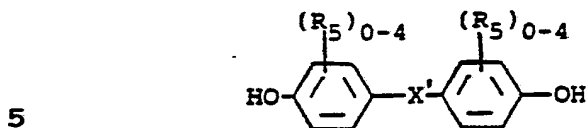
- and R_1 and R_2 are C_1 to C_4 alkyl or alkoxy groups and can be the same or different, and (b) from about 1 to about 20 percent by weight of a second poly(aryl ether sulfone) having a T_g lower than about 225°C, which poly(aryl ether sulfone) is prepared by the nucleophilic polycondensation reaction of:

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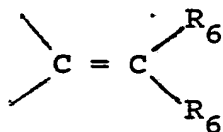
-20-

with bisphenols of the formula:



wherein X' is selected from the group consisting of
 10 alkylene and alkylidene radicals having up to and inclusive eight carbon atoms, cyclo-alkylene and cycloalkylidene radicals having up to and inclusive nine carbon atoms, S, CO, and the radicals:

15

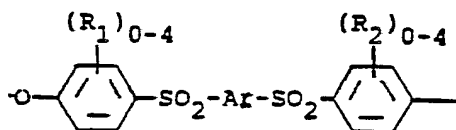


20 the R₅'s are hydrogen or C₁ to C₄ alkyl or alkoxy radicals or halogen atoms and can be the same or different; the R₆'s are hydrogen or C₁ to C₄ alkyl radicals or halogen atoms and can be the same or different.

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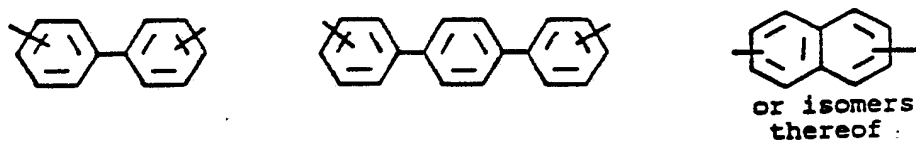
2. A composition as defined in Claim 1 wherein the
 poly(aryl ether sulfone) having a Tg higher than about
 240°C contains at least 50 mole percent of units of
 30 formula

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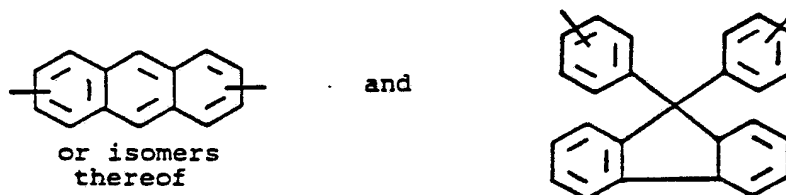


wherein Ar is selected from the group of

-21-



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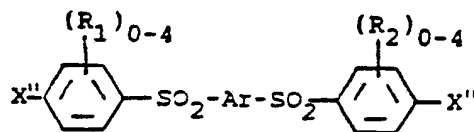
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and R_1 and R_2 are C_1 to C_4 alkyl or alkoxy groups and can be the same or different.

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3. A composition as defined in Claims 1 or 2 wherein the poly(aryl ether sulfone) having a T_g higher than about 240°C is prepared by the nucleophilic polycondensation of the dihalo-compound of formula

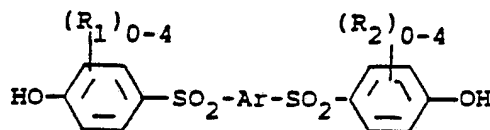
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with the diphenol of formula

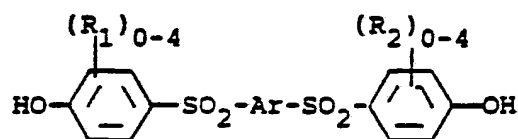
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35 wherein X'' is a halogen and Ar, R_1 and R_2 are as previously defined, and/or with any other dihydric phenol or mixture of dihydric phenols.

4. A composition as defined in Claims 1 or 2 wherein the poly(aryl ether sulfone) having a Tg higher than about 240°C is prepared by the nucleophilic polycondensation of the diphenol of formula

5



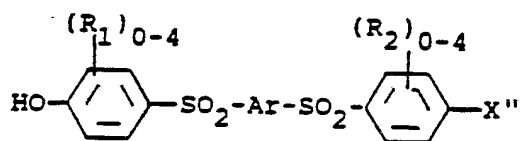
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wherein Ar, R₁ and R₂ are as previously defined, with an activated dihalobenzenoid or dinitrobenzenoid compound or mixtures of these compounds.

15

5. A composition as defined in Claims 1 or 2 wherein the poly(aryl ether sulfone) having a Tg higher than about 240°C is prepared by the base catalyzed self-condensation of the halophenol of formula

20



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wherein Ar, R₁, R₂ and X'' are as previously defined, optionally in the presence of a dihydric phenol and an activated dihalo- or dinitrobenzenoid compound.

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6. A composition as defined in Claims 3 or 5 wherein the dihydric phenol is selected from the group of

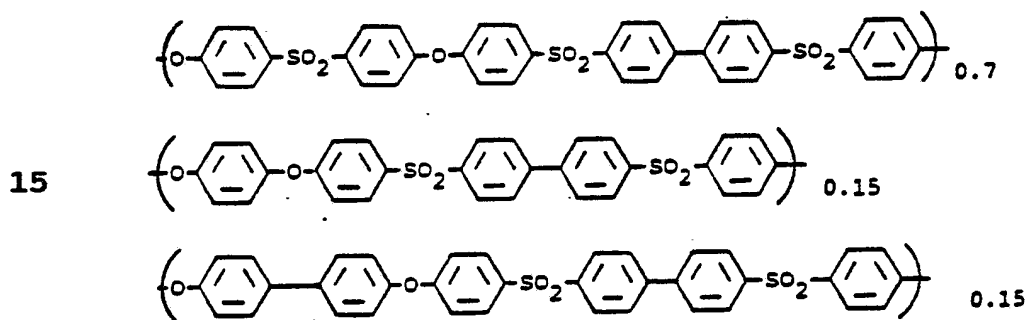
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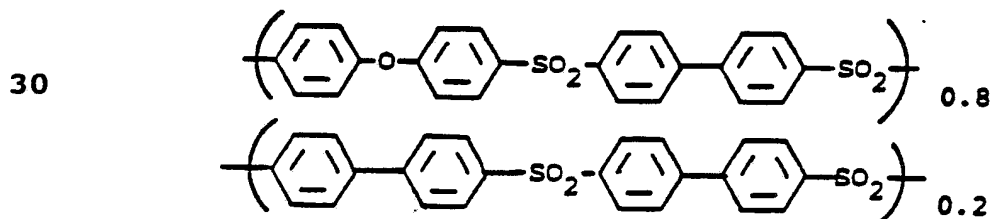
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7. A composition as defined in Claims 1, or 2, or 3, or 6, wherein the poly(aryl ether sulfone) having a T_g higher than about 240°C is a random terpolymer of the following structure:



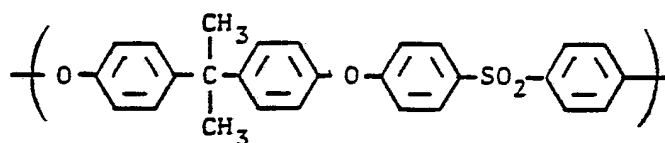
8. A composition as defined in Claims 1 or 2 wherein the poly(aryl ether sulfone) having a T_g higher than about 240°C is prepared by the electrophilic process.

9. A composition as defined in Claims 1, or 2, or 8, wherein the poly(aryl ether sulfone) having a T_g higher than about 240°C is a random copolymer having the structure:



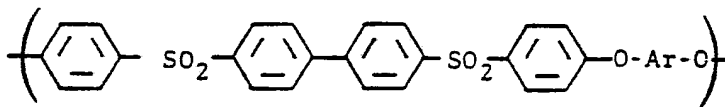
10. A composition according to Claim 1 wherein the poly(aryl ether sulfone) having a T_g lower than about 225°C

-24-



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11. A composition according to Claim 1 wherein the poly-
 10 (aryl ether sulfone) having a Tg higher than about 240°C
 is of the structure:



15

wherein Ar is a mixture of phenylene and diphenylene.

- 20 12. An immiscible blend of poly(aryl ether sulfone)
 polymers comprising:

a) from about 80 to about 99 weight percent of
 poly(aryl ether sulfone) polymer having a Tg higher than
 25 about 240°C, and

b) from about 1 to about 20 weight percent of a
 poly(aryl ether sulfone) having a Tg lower than about
 225°C.


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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US88/02541

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL. (4) C08G 8/02 C08G 14/00 US. CL. 528/125, 126, 128, 174, 219; 525/150, 390		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
U.S.	528/125; 528/126; 528/128; 528/174; 528/219 525/150; 525/390	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 3,634,355 21 MARCH 1968, (BARR ET AL) SEE ENTIRE DOCUMENT.	1-12
A	US, A, 3,647,751 07 MARCH 1972, (DARSOW ET AL), SEE ENTIRE DOCUMENT.	1-12
A	US, A, 4,358,569 09 NOVEMBER 1982, (QUINN ET AL), SEE ENTIRE DOCUMENT.	1-12
A	US, A, 4,503,168 05 MARCH 1985 (HARTSING Jr.). SEE ENTIRE DOCUMENT	1-12
<div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
L@ 12 SEPTEMBER 1988		22 NOV 1988
International Searching Authority		Signature of Authorized Officer
ISA/US		 MARVIN L. MOORE

DERWENT-ACC-NO: 1989-061148

DERWENT-WEEK: 199512

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TITLE: Poly(aryl ether sulphone) blends with improved flow properties made from immiscible polysulphone(s) with different glass transition temps., and retaining properties of components

INVENTOR: HARRIS J E

PATENT-ASSIGNEE: AMOCO CORP[STAD]

PRIORITY-DATA: 1987US-078460 (July 27, 1987) , 1989WO-US02541 (February 13, 1989)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE
WO 8901003 A	February 9, 1989	EN
US 4818803 A	April 4, 1989	EN
EP 327634 A	August 16, 1989	EN
JP 02500849 W	March 22, 1990	JA
US 4957978 A	September 18, 1990	EN
EP 327634 B1	September 22, 1993	EN
DE 3884373 G	October 28, 1993	DE
EP 327634 A4	September 5, 1990	EN

DESIGNATED-STATES: JP US AT BE CH DE FR GB IT LI NL
SE AT BE CH DE FR AT BE CH DE FR
GB IT LI LU NL SE

APPLICATION-DATA:

PUB-NO	APPL- DESCRIPTOR	APPL-NO	APPL-DATE
WO1989001003A	N/A	1988WO- US02541	July 27, 1988
EP 327634A	N/A	1987EP- 907470	July 27, 1987
US 4818803A	N/A	1987US- 078460	July 27, 1987
EP 327634A4	N/A	1988EP- 907470	July 27, 1988
DE 3884373G	N/A	1988DE- 3884373	July 27, 1988
EP 327634B1	N/A	1988EP- 907470	July 27, 1988
JP 02500849W	N/A	1988JP- 506859	July 27, 1988
EP 327634B1	N/A	1988WO- US02541	July 27, 1988
DE 3884373G	N/A	1988WO- US02541	July 27, 1988
US 4957978A	Based on	1989US- 344289	February 13, 1989

INT-CL-CURRENT:

TYPE	IPC DATE
CIPP	C08L71/10 20060101
CIPS	C08G65/38 20060101
CIPS	C08G65/40 20060101
CIPS	C08L71/12 20060101
CIPS	C08L81/00 20060101
CIPS	C08L81/06 20060101

ABSTRACTED-PUB-NO: WO 8901003 A

BASIC-ABSTRACT:

Immiscible blend of poly(aryl ether sulphone) (PAES) polymers is claimed which comprises (a) 80-99 wt.% of a PAES polymer with Tg above 240 deg.C and pref. comprising units of formula (I) Ar = biphenylene, terphenylene, naphthylene, anthracenylene or fluorene-9,9-bis(phenylene); and R1 and R2 = 1-4C alkyl or alkoxy; and (b) 1-20 wt.% of a second PAES polymer with Tg below 225 deg.C and pref. prepd. by nucleophilic polycondensation of 4,4'-dichlorodiphenyl sulphone with bisphenols of formula (II). X1 = alkyl(id)ene of up to and including 8C, cycloalkyl(id)ene of up to and including 9C, S, CO or a gp. of formula (III). R5 = H, 1-4C alkyl or alkoxy or halogen; and R6 = H or 1-4C alkyl.

USE/ADVANTAGE - Blends have improved flow properties compared to prior art high Tg PAES materials, the lower Tg constituent tending to migrate to the wall and act as a lubricant. The good mech. properties of the constituents are retained and the heat distortion temp. of the high Tg component is practically unaffected by addn. of the low Tg component. The blends can be shaped to give mouldings, coatings, films or fibres; they are esp. used as elec. conductor insulation.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: POLY ARYL ETHER SULPHONE BLEND
IMPROVE FLOW PROPERTIES MADE
IMMISCIBLE POLYSULPHONE GLASS
TRANSITION TEMPERATURE RETAIN
COMPONENT

DERWENT-CLASS: A25 A85 F01 X12

CPI-CODES: A05-H07; A05-J06; A07-A03; A07-A03C; F01-D10;

EPI-CODES: X12-D03; X12-E02B;

POLYMER-MULTIPUNCH-CODES-AND-KEY-SERIALS:

Key Serials:

0004	0016	0029	0036	0203	0206	0207
0211	0218	0219	0222	0226	1279	1309
1365	1367	1369	1373	1375	1377	1383
1867	1920	1962	2064	2148	2152	2172
2315	2318	2513	2524	2545	2551	2556
2572	2667	2718	2727	2737	3083	3085
3087						

Multipunch Codes:

02&	038	040	05-	062	080	147	151	153
163	197	213	217	218	219	220	221	222
223	225	262	311	314	316	344	346	355
400	42-	435	444	476	477	481	506	509
512	531	532	536	546	57&	58&	59&	604
608	623	627	681	721				

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: 1989-027070

Non-CPI Secondary Accession Numbers: 1989-046551